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(54) Title: CELLULOSE/POLYMER COMPOSITE ENTHALPY EXCHANGER AND METHOD FOR ITS MANUFACTURE

(57) Abstract

The invention relates to a composite enthalpy exchanger useful for transferring or removing latent and sensible heat from a gaseous stream. This enthalpy exchanger consists of a cellulose-based substrate impregnated with a polymeric desiccant. Also provided is a method of manufacture of the enthalpy exchanger wherein the process for synthesizing the polymer on the substrate is disclosed.

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CELLULOSE/POLYMER COMPOSITE ENTHALPY EXCHANGER AND METHOD FOR ITS MANUFACTURE

Technical Field

The invention relates to a new sensible and latent heat exchange device, hereinafter termed an enthalpy exchanger, and to a method for its manufacture. This enthalpy exchanger consists of a cellulose-based substrate impregnated with a polymeric desiccant. This device has possible applications in the field of air treatment, such as dehumidification, in systems for the transfer of moisture and heat between two air streams, in HVAC systems and in other applications involving water vapour control and recovery.

10 Background Art

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The solid desiccants used in air treatment systems or other applications are primarily inorganic (silica gel, molecular sieves, etc). They take the form of fine powders which must be bonded to a rigid substrate. There are a number of techniques for depositing these desiccants, some of which have been patented. Examples include patents filed in the United States under Nos. 3,338,034; 4,769,053; 5,052,188; 5,120,694; and 5,496,397. U.S. Patent No. 5,542,968 describes a method which involves mixing the desiccant powder with fibres in a solution containing a binder and fire retardants, among other ingredients. A manufacturing process borrowed from the paper industry is then used to produce sheets of this compound.

Another technique disclosed in Canadian Patent No. 1,285,931 involves coating a metallic substrate with a mixture consisting primarily of an inorganic desiccant and a heat-curable binder or adhesive in a solvent. The powder is then bonded to the substrate by heating the article. U.S. Patent No. 4,172,164 describes the use of a solvent to dissolve the surface of the thermoplastic substrate, leaving the polymer particles imbedded in it following evaporation of the solvent. These techniques have the disadvantage of inhibiting to some extent the absorption of water by the desiccant powder, which may deliquesce and become detached under conditions of actual use.

Summary of the Invention

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The technique presented here involves the production of an enthalpy exchanger consisting of a cellulose substrate coated with a polymerized desiccant. Polymer-based desiccants have the advantage of being readily modified to obtain the desired absorptive properties, as well as other properties of interest for certain applications. The polymers themselves have relatively good thermal transfer properties thereby enabling sensible heat transfer. They can also be obtained in a number of geometric forms. Some have a certain affinity for structural products used as substrates, which can facilitate bonding.

The product developed consists, preferably, of a potassium salt of acrylic acid polymerized on a corrugated cardboard substrate. The technique used to bond the desiccant to the substrate does not alter the properties of the desiccant, even when the proportion of polymer by mass is relatively low. In addition, the article has good fire resistance and acceptable mechanical strength.

In this application, applicants are also seeking a high rate of absorption and desorption, so that the article reacts rapidly to a sudden variation in the concentration of water vapour or other gases in the flow of air in contact with the desiccant. Deposition of the polymer in a thin layer on the walls of the substrate makes it possible to obtain very rapid sorption kinetics. Controllable swellability permits repeated cycles of water vapour absorption and desorption.

In general, the technique consists of preparing a solution with a base of acrylic, methacrylic or itaconic acid or a mixture thereof. The monomer is mixed with a sufficient quantity of a homolytic reaction initiator such as a peroxide, azabisisobutyronitrile or other initiator, in water, acetone and/or other solvents. A cross-polymerization agent such as trimethylolpropane triacrylate, divinylbenzene or other cross-polymerization agent is added to the solution in a quantity corresponding to the desired density of cross-linkages to be obtained in the polymer. The solution is well mixed, then applied to the cellulose-based exchanger. Cellulose has been selected because of its chemical affinity for polymer. The article, impregnated with the solution, is placed in a chamber with low oxygen and heated to a temperature of between 50°C and 80°C. The polymerization reaction thus initiated should be completed within a few minutes, depending on the rate of thermal exchange in the chamber. Once the polymerized

solution is bonded to the substrate, the polymer is placed in contact with a hydroxide solution of sodium, potassium, lithium or other monovalent or bivalent cations. The polymer is transformed into a salt. The substrate and desiccant may then dried to form a rigid article.

When the desiccant absorbs water vapour or other products, its volume increases. In certain applications, the swelling may be excessive and must be controlled or minimized. This can be done by simply adjusting the proportions of the products used in the composition of the polymer, such as the cross-polymerization agent. The swelling of the polymer is, in fact, related to the degree of cross-linkage.

The concentration of the base monomer in the solution can be adjusted on the basis of the desired proportion of desiccant by mass to be obtained. Generally, the amount of polymer present in the article or substrate is from about 5 to 65% by mass, and preferably from about 15 to 30% by mass.

The enthalpy exchanger contains passageways which allow the air to circulate and to come into contact with the substrate walls and the desiccant. The enthalpy exchanger permits exchanges of sensible heat and moisture with an air stream. It may be a rotary or static type with parallel or cross streams. The first case involves wall-to-air exchanges of sensible and latent heat while, in the second, heat and moisture pass through the wall of the exchanger for transfer from one air stream to another.

The enthalpy exchanger of the present invention can be manufactured by either of two techniques. The first consists of constructing the exchanger in its final form and impregnating it with the monomer solution, which is then polymerized. The exchanger can be constructed by rolling the substrate to form a wheel, or by stacking the substrate to produce a static exchanger with cross or parallel streams. The substrate may consist of corrugated cardboard, corrugated paper or any other cellulose-fibre-based product. The second technique involves impregnating a continuous flat sheet of cellulose-based substrate with the monomer solution, which is then polymerized. The composite sheet thus obtained is corrugated before drying to obtain the desired passageway geometry, then rolled to form a wheel, for example.

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The technique used to bond the desiccant to the substrate does not affect the desiccant's absorptive properties. This process does not alter the desiccant's absorptive properties. In addition, it gives the substrate a number of other interesting properties, including mechanical rigidity and fire resistance. Due to the thermal properties of the polymer, the desiccant article is also capable of transferring heat from a warm air (gas) stream to a cool air (gas) stream within a recovery system. The bond obtained between the desiccant and the substrate is very strong and permits it to withstand a large number of absorption and desorption cycles without any deterioration in absorptive properties or physical characteristics. A further advantage of this technique is the fact that these properties can be controlled by adjusting the composition and quantity of polymer. Most supports made from natural or synthetic cellulose fibres are permeable to air, which can pose a contamination problem in certain applications such as air exchangers. Treatment of this type of support with the polymer makes it much more air-tight and also more rigid, even using amounts of the polymer on the order of only 10%. For an application in the field of total heat exchangers made from paper or cardboard, a quantity of polymer on the order of 15% to 20% of total mass has been found to result in a product with very good sorption capacity and kinetics, good mechanical resistance as well as very good fire resistance (non-flammability). Furthermore, it is believed that the product has bactericidal properties and that it transfers virtually none of the contaminants present in the air. These last two properties are particularly important for applications in the domestic sector.

Cellulosic-based substrates are desirable due to its chemical affinity for polymer and its low cost. Preferably, the support is made from corrugated cardboard or paper due to the high quality/price ratio. However, other types of substrate made from natural or synthetic fires, woven or non-woven, can be used. The polymer has also been successfully deposited on silica-gel powder in order to fix it by some other technique, such as gluing on to substrates made of metal or plastic material. Other inorganic powders (talc, etc.) or organic powders (skeletons of micro-organisms, etc.) can also be used.

The monomer solution consists primarily of a member of the carboxylic acid family such as acrylic acid or methacrylic acid, a homolytic reaction initiator such as peroxide, and a cross-polymerization agent such as trimethylolpropane triacrylate. The mixture is soluble in water and/or a solvent such as acetone.

Following impregnation with the solution, the substrate is heated in a chamber with very low oxygen to a temperature of between 50°C (122 °F) and 80°C (176°F).

The acidic polymer is then placed in contact with an alkaline solution of sodium, potassium or other hydroxide, to transform it into a salt of these cations. This operation gives the polymer, and thus the enthalpy exchanger, its absorptive properties.

Best Mode for Carrying Out the Invention

The process of applying the polymeric desiccant material to the cellulosic substrate as either a stock material or as a pre-constructed article made from a cellulosic substrate is generally carried out in the same manner. The process consists of preparing a monomer solution with a base of acrylic, methacrylic or itaconic acid or a mixture thereof. The concentration of the base monomer in the solution can be adjusted on the basis of the desired proportion of desiccant by mass to be obtained. In the preferred embodiment, acrylic acid is used. The quantity of acrylic acid should be between 2.5M and 4.0M; at less than 2.5M, the gel obtained will be insufficiently rigid, and above 4.0M, there is a risk of the reaction being too violent (exothermic) and thus difficult to control. Between 20% and 90% of the carboxyl groups must be neutralized by the addition of potassium hydroxide (KOH) or another base. Preferably, 50% of the carboxyl groups must be neutralized by adding a solution of KOH dissolved in water. The total quantity of water in the final solution must not exceed 35% of the overall volume. A greater volume of water would risk destroying the structure of the cellulosic fibre support and would limit the maximum quantity of dissolved cross-polymerizing agent.

The monomer is then mixed with a sufficient quantity of a homolytic reaction initiator such as a peroxide, azabisisobutyronitrile or other initiator, in water, acetone and/or other solvents. Other possible choices of initiator include a peroxide such as sodium, ammonium or potassium persulphate, a hydroxyperoxide such as cumene hydroxyperoxide or an alkyl peroxide such as di-tert-butylperoxide. Peroxide is preferred because of its non-toxicity and low cost. The amount of reaction-initiating agent must be sufficient to start the reaction, that is, about 1% of the total solution volume, although an excess of this substance would have no impact on the polymerized product.

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A cross-polymerization agent such as trimethylolpropane triacrylate, propane ethoxylate, triacrylate, divinyl benzene or other cross-polymerization agent is added to the solution in a quantity corresponding to the desired density of cross-linkages to be obtained in the polymer. To obtain an article capable of absorbing enough water vapour without excessive swelling, it is necessary to use 0.1% to 2.0% by volume of a cross-polymerizing agent, preferably trimethylolpropane triacrylate. Trimethylolpropane triacrylate is preferred because of its cost. A proportion on the order of 1% of total volume has been found to produce the best compromise for the desired properties in an enthalpy exchanger. The increase in volume (or swelling) of the desiccant material as a result of the absorption of water vapour can be controlled by the proportion of cross-polymerization agent used to synthesize the polymer.

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A quantity of organic solvents (acetone, for example) must be added to bring about complete solution. Other solvents may be used or mixed with the acetone. In order to minimize loss of acrylic acid during the heating phase, it is possible to use propylene glycol, ethylene glycol or other solvents compatible with acetone and having a high boiling point.

The solution is well mixed, then applied to the cellulose-based substrate or the pre-constructed article. The article, impregnated with the solution, is placed in a closed chamber containing minimum oxygen and heated to a temperature sufficient to initiate polymerization. The polymerization reaction thus initiated should be completed within a few minutes, depending on the rate of thermal exchange in the chamber. Since polymerization is a radical reaction which is blocked in the presence of oxygen, it is therefore preferable to minimize the amount of oxygen in the solution in order to avoid the formation of short-chain molecules or a poor polymerization yield. The presence of minute quantities of oxygen should have no perceptible effect on the quality of polymerization. In practice, purging with a flow of nitrogen or argon is usually sufficient to displace any oxygen dissolved in the solution or present in the dead space around the article.

Heating temperature must be sufficient to initiate polymerization, but must not lead to excessive evaporation of the acrylic acid. A temperature of 80°C to 120°C is suggested. Preferably, the heating equipment will be sufficiently powerful to minimize the heating time.

High-frequency or microwave ovens are especially recommended, but a sufficiently powerful conventional oven can be used effectively and can reduce manufacturing costs.

The extent of cross-linkage is fixed by the amount of cross-polymerizing agent which has actually reacted during the polymerization. To that end, it is important to ensure that it is uniformly and completely dissolved in the monomer solution. In the present case, where the preferred agent is trimethylolpropane triacrylate which has limited aqueous solubility, it is necessary to use organic solvents such as acetone, propylene glycol as well as other compatible solvents. The organic solvents promote improved solubility of the cross-polymerizing agent, which makes it possible to obtain a polymeric gel with a three-dimensional structure. It is preferable to limit the volume of water to 35% of the total volume of monomer solution.

Once the polymerized solution is bonded to the substrate, the polymer is placed in contact with a hydroxide solution of sodium, potassium, lithium, ammonium or other monovalent or bivalent cations. The polymer is transformed into a salt of the cation corresponding to the alkaline solution used to give the polymer its absorptive properties. In the preferred embodiment, the acrylic acid based polymer is converted to a polyacrylic acid salt by wetting the article with a solution of potassium hydroxide or sodium hydroxide dissolved in methanol. Potassium hydroxide is preferred as it gives the polymer better absorptive properties.

The treated article or substrate is then dried or allowed to dry, if necessary. In the case of the polymerization treatment being applied to a substrate, the substrate is then used generally as stock material in the fabrication of the enthalpy exchanger's "working" components.

An illustration of the principles of the present invention is provided by way of the following example.

EXAMPLE

An enthalpy-exchange wheel containing 20% by mass of the polymer obtained by starting with a solution of 2.5M of acrylic acid in 250 ml of aqueous KOH, with 1% by volume of trimethylolpropane triacrylate, 1% by volume of peroxide and the rest acetone by volume, the absorption capacities are 30%, 40% and 95% in the presence of a flow of air with a relative

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humidity of 30%, 60% and 90% respectively. The wheel exhibits a high rate of absorption and desorption and reacts rapidly to a sudden variation in the concentration of water vapour or other gases in the flow of air in contact therewith. Tests carried out with full-size enthalpy exchangers showed that the polymer has very good sorption kinetics for water vapour, even under extreme conditions of use.

It will be understood from the foregoing that the example and embodiments referred to herein are intended to be illustrative of the principles of the invention and should not be construed as limiting. Those skilled in the art will appreciate that various modifications and/or substitutions in both the materials and the method can be effected without departing from the spirit and scope of the invention as defined in the appended claims.

Industrial Applicability

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The enthalpy exchanger in accordance with the present invention has possible applications in the field of air treatment, such as dehumidification, in systems for the transfer of moisture and heat between two air streams, in HVAC systems and in other applications involving water vapour control and recovery.

21. The enthalpy exchanger of claim 18, wherein the alkyl peroxide is di-tert-butylperoxide.

- 22. The enthalpy exchanger of one of claims 2, 10, 11 or 12, wherein the cross-polymerization agent is trimethylolpropane triacrylate, divinylbenzene or a compatible cross-polymerization agent.
- 23. The enthalpy exchanger of claim 2, wherein the carboxylic acid, the cross-polymerization agent and the homolytic reaction initiator are dissolved in a solution of water and solvent.
- 24. The enthalpy exchanger of claim 23, wherein the solvent is organic.
- 10 25. The enthalpy exchanger of claim 24, wherein the solvent is selected from the group consisting of acetone, acetic acid, benzene, ethyl acetate or any combination thererof.
 - 26. A method of making an enthalpy exchanger of a predetermined structure comprising the steps of:
- (a) wetting a cellulose-based substrate with a solution containing a polymerizable
 monomer, a homolytic reaction initiator, a cross-polymerization agent and one or more solvents;
 - (b) heating the wetted substrate in an environment sufficiently low in oxygen to effect polymerization of the monomer;
 - (c) treating the substrate in an alkaline solution to transform the polymer into a salt;
 - (d) drying the treated substrate at a temperature lower than the temperature of decomposition of the polymer; and
 - (f) fabricating the dried, treated substrate into said predetermined structure.
 - 27. The method of claim 26, wherein the heating step (b) is carried out in a closed low- or no-oxygen chamber.

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28. The method of claim 27, wherein the atmosphere of the chamber is controlled through the use of a vacuum or an inert gas such as nitrogen or argon.

- 29. The method of claim 26, wherein the heating step (b) is carried out a temperature of between 50°C and 80°C.
- 5 30. The method of claim 26, wherein the heating step (b) is carried out in an electrical or microwave oven.
 - 31. The method of claim 26, wherein the substrate comprises corrugated cardboard sheets which, when treated and dried, are rolled around a hub to form a wheel with transverse parallel passageways.
- The enthalpy exchanger of claim 26 wherein the monomer is acrylic acid which is present in the solution in a concentration between 2.5M to 4.0M.
 - 33. The enthalpy exchanger of claim 32 wherein the amount of homolytic reaction initiator in the solution is about 1% by volume.
- 34. The enthalpy exchanger of claim 32 or claim 33 wherein the amount of cross-polymerization agent in the solution is between 0.1-2% by volume.
 - 35. The enthalpy exchanger of one of claims 32, 33 or 34 wherein the solvent is water and/or acetone.
 - 36. The enthalpy exchanger of claim 13 wherein the amount of water is less than 35% by volume of the solution.
- 20 37. A method of making an enthalpy exchanger of a predetermined structure comprising the steps of:
 - (a) pre-fabricating a cellulose-based substrate generally into the form of said predetermined structure;

10. The enthalpy exchanger of claim 2 wherein the monomer is acrylic acid which is present in the solution in a concentration between 2.5M to 4.0M.

- 11. The enthalpy exchanger of claim 10 wherein the amount of homolytic reaction initiator in the solution is about 1% by volume.
- 5 12. The enthalpy exchanger of claim 10 or claim 11 wherein the amount of cross-polymerization agent in the solution is between 0.1-2% by volume.
 - 13. The enthalpy exchanger of one of claims 10, 11 or 12 wherein the solvent is water and/or acetone.
- 14. The enthalpy exchanger of claim 13 wherein the amount of water is less than 35% by volume of the solution.
 - 15. The enthalpy exchanger of one of claims 10 to 14, wherein the homolytic reaction initiator is soluble in water.
 - 16. The enthalpy exchanger of one of claims 10 to 15, wherein the homolytic reaction initiator is a peroxide.
- 15 17. The enthalpy exchanger of claim 16, wherein the peroxide is sodium, ammonium or potassium persulphate.
 - 18. The enthalpy exchanger of claim 16, wherein the peroxide is a hydroxyperoxide.
 - 19. The enthalpy exchanger of claim 18, wherein the hydroxyperoxide is cumene hydroxyperoxide.
- 20 20. The enthalpy exchanger of claim 16, wherein the peroxide is an alkyl peroxide.

WE CLAIM:

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1. An enthalpy exchanger comprising a cellulosic-fibre-based substrate having coated thereon or impregnated therein a polymeric desiccant.

- 2. The enthalpy exchanger of claim 1, wherein the polymeric desiccant is obtained by polymerization of a solution applied to said substrate containing a monomer of the carboxylic acid family, a homolytic reaction initiator and a cross-polymerization agent, dissolved in a mixture of water and solvent and subsequently transforming the polymer into a salt.
 - 3. The enthalpy exchanger of claim 2, wherein the polymer present in the substrate represents a proportion of from 5% to 65% by mass.
- 10 4. The enthalpy exchanger of claim 3, wherein the polymer present in the substrate represents a proportion of from 15% to 30% by mass.
 - 5. The enthalpy exchanger of claim 1, wherein the substrate is a fibrous material of natural cellulose fibres or organic synthetic fibres.
- 6. The enthalpy exchanger of claim 5, wherein the substrate is corrugated or uncorrugated cardboard.
 - 7. The enthalpy exchanger of claim 5, wherein the substrate is paper or filter paper.
 - 8. The enthalpy exchanger of claim 2, wherein the polymeric desiccant contains at least one polymer of the family of unsaturated carboxylic acids.
- 9. The enthalpy exchanger of claim 2, wherein the polymeric desiccant contains at least one polymer derived from polyacrylic acids, polymethacrylic acids or a compound containing a mixture thereof.

INTERNATIONAL SEARCH REPORT

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Intern: al Application No PCT/UA 99/00215

PCT/CA 99/00215 . CLASSIFICATION OF SUBJECT MATTER PC 6 B01D53/04 B01D B01D53/28 B01J20/26 B01J20/32 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01D B01J F28F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X PATENT ABSTRACTS OF JAPAN vol. 005, no. 083 (M-071), 30 May 1981 1,5,7-9 & JP 56 030595 A (MITSUBÍSHI ELECTRIC CORP), 27 March 1981 Α see abstract 2,26,37 X PATENT ABSTRACTS OF JAPAN vol. 005, no. 010 (M-051), 22 January 1981 1,5,7 & JP 55 140097 A (MITSUBÍSHI ELECTRIC CORP), 1 November 1980 Α see abstract 2,26,37 Α US 4 948 659 A (ITOH KIICHI ET AL) 14 August 1990 1,2,26, see column 3, line 28 - line 41 see column 6, line 41 - line 61; claim 1 Further documents are listed in the continuation of box C. X Patent family members are listed in annex. Special categories of cited documents: T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-ments, such combination being obvious to a person skilled in the art. "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 16 June 1999 25/06/1999 Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 Nt. - 2280 HV Rijswijk Tel. (431-70) 340-2040, Tx. 31,651 apo nt Authorized officer Fax: (+31-70) 340-3016 ~Farria.⊸C Form PCT/ISA/210 (second sheet) (July 1992)

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C.(Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 605 401 A (CHMELIR MIROSLAV ET AL) 12 August 1986 see example 11	1,2,26,
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45. The enthalpy exchanger of claim 44 wherein the amount of homolytic reaction initiator in the solution is about 1% by volume.

- 46. The enthalpy exchanger of claim 44 or claim 45 wherein the amount of cross-polymerization agent in the solution is between 0.1-2% by volume.
- 5 47. The enthalpy exchanger of one of claims 44, 45 or 46 wherein the solvent is water and/or acetone.
 - 48. The enthalpy exchanger of claim 47 wherein the amount of water is less than 35% by volume of the solution.

(b) preparing a solution containing a polymerizable monomer, a homolytic reaction initiator, a cross-polymerization agent and one or more solvents;

- (c) wetting the surfaces of the pre-fabricated structure with the solution of step (b);
- (d) heating the wetted pre-fabricated structure in an environment sufficiently low in oxygen to effect polymerization of the monomer;
- (e) treating the pre-fabricated structure in an alkaline solution to transform the polymer into a salt; and
- (f) drying the treated pre-fabricated structure at a temperature lower than the temperature of decomposition of the polymer.
- 10 38. The method of claim 37, wherein the heating step (d) is carried out in a closed low- or no-oxygen chamber.
 - 39. The method of claim 38, wherein the atmosphere of the chamber is controlled through the use of a vacuum or an inert gas such as nitrogen or argon.
- 40. The method of claim 37, wherein the heating step (d) is carried out a temperature of between 50°C and 80°C.
 - 41. The method of claim 37, wherein the heating step (d) is carried out in an electrical or microwave oven.
 - 42. The method of claim 37, wherein the pre-fabricated structure comprises corrugated cardboard sheets which are rolled around a hub to form a wheel with transverse parallel passageways.
 - 43. The method of claim 37, wherein step (c) is effected by immersing the pre-fabricated structure into said solution.
 - 44. The enthalpy exchanger of claim 37 wherein the monomer is acrylic acid which is present in the solution in a concentration between 2.5M to 4.0M.

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INTERNATIONAL SEARCH REPORT

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Interr had Application No PCT/CA 99/00215

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